DESORPTION AND CRYOGENIC RECOVERY OF VOLATILE ORGANIC COMPOUNDS FOR RE-USE

K.R. Carmichael, M. Lordgooei, T.W. Kelly, M.J. Rood, S.M. Larson
Department of Civil Engineering / Environmental Engineering Program
University of Illinois at Urbana-Champaign
205 N. Mathews St.
Urbana, Illinois U.S.A. 62801-2352

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Introduction

Both the magnitude and toxicity of emissions of volatile organic compounds (VOCs) have led to public health concern and recent government regulations to reduce VOC emissions. VOCs are a part of the 1.1×10^9 kg of toxic chemicals released into the atmosphere from point sources within the United States in 1990 [1]. VOCs appearing on the list of 189 hazardous air pollutants (HAPs) accounted for 4.5×10^8 kg/yr of emissions to the atmosphere [1]. Many of these toxic chemicals cause chronic and acute health effects, including cancer [2].

The 1990 Clean Air Act Amendments (CAAAs) established technology-based guidelines for the reduction of VOC emissions to the atmosphere from point sources [3]. Under Title I of these amendments, USEPA is required to establish reasonable achievable control technology (RACT) standards for point source VOC emissions in ozone related non-attainment areas. Furthermore, Title III requires USEPA to establish maximum achievable control technology (MACT) standards for point source emissions of 189 HAPS, many of which are considered VOCs. HAP emission standards for point sources based on MACT must be promulgated by November 15, 2000. Sources regulated under Title III must meet permit requirements within three years of promulgation.

Point source VOC emission reduction is generally accomplished by process modification and/or utilization of ancillary control devices [4]. Process modification is generally the most economical method of reducing VOC emissions. Further reduction of VOC emissions require the addition of control devices along the waste stream.

The seven most widely used control devices that remove VOCs from gas streams are: 1) thermal incinerators, 2) catalytic incinerators, 3) flares, 4) boilers/process heaters, 5) carbon adsorbers, 6) absorbers and 7) condensers [5] (Table 1).

Table 1. Control devices commercially available for VOC removal from effluent gas streams [4].

Control Device	VOC Content (ppmv)	Flow Rate (acfm)	Capital Cost 1993	Annual Cost 1993	Removal Efficiency	Advantages	Disadvantages
Thermal Incinerator	100-2000*	1000 to 500,000	$10 to 450/cfm	$15 to 150/cfm	95-99+%	Up to 95% energy recovery	Halogenated compounds may require additional control
Catalytic Incinerator	100-2000*	1000 to 100,000	$20 to 250/cfm	$10 to 90/cfm	90-95%	Up to 70% energy recovery	Catalyst poisoning
Flare [5]		<2,000,000			>98% Steam-assisted	VOC destruction of variable emission conditions	Low heating value VOC requires auxiliary fuel
Boiler [5]		Steady			>98%	Supplement fuel	Variations may affect process
Carbon Adsorber	20-5000*	100 to 60,000	$15 to 120/cfm	$10 to 35/cfm	90-98%	Vapor recovery, Pre-Concentrator	High RH may lower capacity, Pore fouling
Absorber	500-5000	2000 to 100,000	$15 to 70/cfm	$25 to 120/cfm	95-98%	Vapor recovery	Scale build-up, Liquid waste
Condenser	>5000	100 to 20,000	$10 to 80/cfm	$20 to 120/cfm	50-90%	Vapor recovery	Scale build-up, Liquid waste

* <25% of lower explosion limit; RH is relative humidity

In this paper, discussion will primarily pertain cryogenic condensation of VOCs during regeneration of a carbon adsorber used to concentrate VOCs in effluent gas streams. Condensation of VOCs is especially applicable when recovery and reuse of the VOC in the process stream is economically beneficial. Recovery should be considered when a relatively pure condensate with a monetary value > $0.66/kg can be recovered [6].

Adsorption has been used often as a pre-concentrator in conjunction with other control devices. This is especially applicable to condensers as will be discussed here. Carbon adsorbers can remove VOCs from relatively low vapor concentration and high flow rate gas streams and desorb at high vapor concentration and low gas flow rates, where condensers operate more efficiently. High inlet VOC concentrations for condensers yield higher removal efficiencies and require lower refrigerant flow rates, thus lowering operating costs. Low gas flow rates require less condensable surface by increasing residence time, again lowering capital costs. Lower gas flow rates also require less refrigerant to cool the carrier gas.

Design of Contact Condensers

Two general types of condensers are commercially available, direct contact and indirect contact [7]. Direct contact condensers mix the refrigerant with the process gas stream. Heat is more efficiently exchanged due to the intimate contact between the refrigerant and VOC. Direct contact condensation is typically simpler, less expensive to install and requires less auxiliary equipment [7]. However, the refrigerant is

mixed with the process stream. This may prevent refrigerant recycling and/or cause contamination of the refrigerant. Indirect contact condensers utilize a physical barrier across which only heat is exchanged between the refrigerant and the process gas stream. Heat exchange is therefore less efficient in indirect methods. Keeping the refrigerant separate from the process gas stream allows for refrigerant re-use. This is beneficial if the refrigerant undergoes a cyclic mechanical refrigeration process. Indirect contact condensers typically cost more and are more complicated to design and operate [7]. Because of the indirect contactor's advantages, however, it is the most common type of condenser in air pollution control applications [5].

Refrigerants

The most common refrigerant used in pollutant removal condensers is water [5]. Water is inexpensive and easy to handle. However, because the condenser temperature is limited by the refrigerant temperature, cooling water results in low removal efficiencies for many VOCs (Table 2). Removal efficiencies were determined from the reduction of a 10% acetone stream to the equilibrium saturation vapor concentration. For applications where the process stream needs to be cooled below ambient temperatures, the use of cooling water typically requires auxiliary equipment to chill the water prior to use.

Ethylene glycol and water mixtures are also commonly used refrigerants [8]. Lower operating temperatures can be achieved with this mixture than for pure water, thereby lowering the effluent VOC concentration and recovering more condensate. Ethylene glycol water mixtures are exclusively used with indirect contact condensers to prevent ethylene glycol losses to the effluent gas stream [8]. Auxiliary equipment is needed to cool the mixture to temperatures below the ambient temperature.

Liquid nitrogen (LN2) refrigerant can provide a wide range of condenser temperatures because a controlled LN2 flow rate can be delivered to the condenser. Furthermore, because LN2 undergoes a phase change in the condenser, both the enthalpy of vaporization and specific heat change provide cooling capacity. The use of LN2 as a refrigerant generally requires a vacuum jacketed storage vessel and well insulated or vacuum jacketed delivery lines. However, auxiliary cooling equipment is not necessary, as the refrigerant is available in liquid form from commercial sources. The LN2 can be used in direct or indirect contactors. After it passes through the condenser, the vaporized nitrogen refrigerant can be used as a blanket gas in process streams or as a purge stream during desorption if an adsorber is used as a pre-concentrator. The gaseous nitrogen refrigerant waste stream can be used during desorption as a purge stream to prevent explosive hazards and reduce moisture levels, normally present in air purge streams, that may foul the condenser.

By operating the condenser near the freezing point of the organic, very low effluent VOC vapor pressures can be achieved while still producing a liquid condensate. In high humidity process streams two condensers can be used in series. The first condenser can operate at temperatures above the freezing point of water to remove water vapor from the stream. The second condenser can then be operated at temperatures below the freezing point of water to achieve greater removal efficiencies of the organic and reduce condenser fouling from frozen water vapor.

Table 2. Theoretical removal efficiencies for three refrigerants and three VOCs with a 10% by volume inlet gas stream.

Refrigerant	Operating Temperature (K)	Acetone Saturation[a] Vapor Concentration (ppmv)	Acetone Removal Efficiency (%)	Methyl Ethyl Ketone Saturation[a] Vapor Concentration (ppmv)	Methyl Ethyl Ketone Removal Efficiency (%)	Toluene Saturation[a] Vapor Concentration (ppmv)	Toluene Removal Efficiency (%)
Water	278	102,000	0	40000	60	5500	94
60% Ethylene Glycol + H20	240	15000	85	3800	98	420	99+
LN2	200	300	99+	70	99+	2	99+

[a] determined from the Wagner equation [9]

Experimental Design

Our research efforts have focused on developing, testing and evaluating the integration of cryogenic condensation with carbon adsorption. Regeneration of the carbon adsorber provides a concentrated vapor stream at a low gas flow rate which is then sent to the condenser. Using the adsorber as a pre-concentrator improves the operating efficiency of the condenser by increasing removal efficiency and decreasing refrigerant consumption. LN2 was used as the refrigerant due to its' low achievable temperature range and possible re-use capabilities.

A 1% by volume acetone in nitrogen gas stream was passed through an activated carbon cloth fixed bed at 5 slpm (Figure 1). The adsorbent ACC-5092-20 was manufactured by American Kynol™. Nitrogen BET specific surface area is 1592 m^2/g, and its' micropore volume is 0.69 cm^3/g [10]. Apparent ACC bed density is 94.5 mg/cm^3. Equilibrium adsorption capacity of the ACC was found to be 456 mg/g for 1% acetone in nitrogen [10].

The ACC was electrothermally regenerated by applying an a.c. voltage across the cloth. The temperature of the ACC surface was controlled by the voltage. Acetone concentration in the adsorber's effluent was controlled by the bed's temperature and flow rate of nitrogen carrier gas. During regeneration, acetone concentrations greater than 60% by volume were achieved at nitrogen gas flow rates of 0.5 slpm [11].

A copper shell-and-tube indirect contactor was used to condense the concentrated acetone onto the surface walls. The concentrated vapor stream was passed between the condenser tube and the outside shell. The total condensing surface area was 1241 cm^2. LN2 was introduced at the condenser tube inlet

counter current to the vapor laden gas stream. LN2 was also circulated through an 1/8 in. copper tube coil jacket wound around the outside shell of the condenser. LN2 was delivered with a Cryofab self-pressurizing dewar model CFPB25-115. The temperature of the condenser was controlled by the liquid flow rate of LN2. The flow rate of LN2, in turn, was controlled by the pressure of the dewar and by an Asco Red-Hat cryogenic solenoid valve. The vapor laden gas stream temperature was monitored using type T thermocouples at the condenser inlet, mid-point and outlet. The nitrogen refrigerant flow rate was also monitored at the outlet of the condenser using a BIOS DC-2 DRY CAL in continuous operation. Inlet and outlet vapor concentrations were monitored by analyzing 150 μl syringe samples with a Hewlett-Packard GC/MS (GC 5890 Series II, 5971 MS).

Results and Discussion

The ACC fixed bed was integrated with the cryogenic condenser to test acetone removal with condensation. A 1% acetone in nitrogen vapor stream at 5 slpm was passed through the bed at ambient temperatures. At breakthrough, the acetone was desorbed at 1 slpm nitrogen purge stream. The desorbed stream was sent directly to the pre-cooled condenser at ambient temperature and ambient pressure. The condenser log-mean operating temperature was 220 ± 9 K and was at ambient pressure. The acetone vapor concentration at the condenser outlet remained low and fairly constant throughout the desorption cycle (Figure 2). At desorption times between 150 sec. and 1000 sec., the desorbed acetone concentration was greater than the equilibrium vapor saturation concentration. As the vapor cooled in the lines to the condenser, the acetone condensed to the equilibrium vapor concentration of 24% at an ambient temperature of 296 K. The condenser further cooled the vapor to the equilibrium concentration of approximately 0.2 % by volume at 220 K. A removal efficiency of 99.0% was found for the integrated test. During the adsorption/desorption cycle, the acetone in the 1% by volume and 5.0 slpm challenge stream was concentrated up to 60%, and the flow rate was decreased by an order of magnitude [10].

Condenser outlet concentrations were also measured for inlet concentrations ranging from 0.25% to 18.3% by volume (Figure 3) to determine VOC removal efficiencies. The acetone in nitrogen challenge gas stream was generated by passing nitrogen gas through liquid acetone in a dual bubbler set-up. The challenge gas flow rate was 0.5 slpm and at ambient temperature. The condenser was pre-cooled to an equilibrium log-mean temperature of 215 ± 10 K for each experiment. Over the entire range, outlet acetone concentrations remained fairly constant near the equilibrium vapor concentration of 0.17% at 215 K as predicted by the Wagner equation. Removal efficiencies are therefore higher for higher inlet concentrations. For instance, the removal efficiency found for an acetone inlet concentration of 18.3% was found to be 98.8%. However, the removal efficiency for at an inlet of 0.6% was only 70.5%.

Theoretical and experimental LN2 refrigerant requirements were also evaluated (Figure 3). The theoretical mass of LN2 per unit mass of acetone condensed was determined from thermodynamic calculations. At low inlet concentrations, more LN2 is required to condense a unit mass of acetone. For instance, at an inlet concentration of 2.5% by volume acetone, 10 kg of LN2 is theoretically required to condense 1 kg of acetone. However, at an inlet concentration of 20% by volume acetone, only 2 kg of LN2 is required to condense 1 kg of acetone. Experimental results showed the same general trend with deviations from the theoretical curve resulting from heat loss from the condenser. This supports the earlier statement that higher concentration vapor streams result in more efficient recovery of VOC vapor. Therefore at high concentrations the removal efficiency is maximized and the mass of refrigerant per unit mass of acetone condensed is minimized.

The condenser was also evaluated for acetone removal performance at various condenser equilibrium temperatures (Figure 4). A 10% by volume acetone challenge gas stream at 0.5 slpm was sent through the condenser at log-mean temperatures ranging from 209 K to 271 K. The measured outlet concentrations closely approximated the theoretical equilibrium vapor concentration as predicted by the Wagner equation. This indicates that the acetone bulk vapor concentration reached equilibrium with the acetone vapor concentration at the condenser's surface. This would also exist during scale-up if adequate condensing surface is available for the given process stream's vapor concentration, temperature and flow rate.

A model was developed to predict the axial concentration of a vapor along the condenser length. Radial mass transfer was incorporated with the thermodynamic characteristics of the heat exchange between the VOC gas stream and LN2 refrigerant. For a condenser surface area of 1241 cm^2 and process conditions similar to the experimental conditions, equilibrium concentration is predicted at approximately 30 cm for an inlet concentration of 15% acetone (Figure 5). The laboratory condenser is 62.2 cm long. The model can also be used for designing condensers for a specific process gas stream.

Condenser design can be carried out by first determining the process gas stream characteristics such as VOC vapor concentration, temperature and flow rate. By assuming equilibrium conditions, the desired condenser temperature can be determined from the vapor concentration dependence on temperature at the desired outlet concentration. Once the temperature is known, an appropriate refrigerant can be selected. Then by modeling the axial concentration profile, the appropriate surface area and length can be determined from the condensing surface required to reach the desired outlet vapor concentration.

Summary and Conclusions

Integration of a carbon adsorber with cryogenic condensation provides a method to recover VOCs from gas streams in a laboratory scale set-up. Experimental results showed that removal efficiencies of >98% can be achieved for acetone in nitrogen gas streams. Modeling and experimental results also show that condensers operate more efficiently at high VOC concentrations and low gas flow rates. Carbon adsorption can remove relatively low concentration VOCs in high flow rate gas streams and desorb at relatively high concentrations and low flow rates. Carbon adsorption/desorption concentrated a 1% gas stream by over an order of magnitude and decreased flow rates from 5.0 slpm to 0.5 slpm. Condenser removal efficiencies increased from 70.5% to 98.8% for inlet acetone concentrations between 0.6% and 18.3% by volume. The mass of LN2 required to condense a unit mass of acetone was also found to decrease as inlet concentration increased. The Wagner equation proved to be valid for determining the outlet concentration of acetone vapor given the condenser temperature. Cryogenic recovery of VOCs is more efficient when the condenser was integrated with a carbon adsorber.

References

[1]   United States Environmental Protection Agency, *National Air Quality and Emissions Trends Report*, EPA 454/R-93-031, USEPA, 1992.
[2]   McIlvaine, R., Halderman, S. and J. Schwartz *Pollution Engineering*, February 15, 1992, pp. 54-57.
[3]   United States Environmental Protection Agency, 1990 Clean Air Act Amendments, USEPA, 1990.
[4]   Ruddy, E.N. and L.A. Carrol *Chemical Engineering Progress*, July 1993, pp. 28-35.
[5]   United States Environmental Protection Agency, *Control Technologies for Hazardous Air Pollutants*, EPA/625/6-91/014, USEPA, 1991.
[6]   Dyer, J.A. and K. Mulholland *Chemical Engineering*, February 1994, pp. 4-8.
[7]   Buonicore, A.J. and W.T. Davis, Air and Waste Management Association, *Air Pollution Manual*, New York, 1992.
[6]   American Society of Heating, Refrigeration and Air-Conditioning Engineers, *1983 Equipment Volume*, 1983.
[9]   Reid, R.C., Prausnitz, J.M. and T.K. Sherwood *The Properties of Gases and Liquids*, New York, 1977.
[10]   Lordgooei, M., Carmichael, K.R., Kelly T.W., Rood, M.J. and S.M. Larson, Activated Carbon Cloth Adsorption-Cryogenic System to Recover Toxic Volatile Organic Compounds, submitted to Gas Separation and Purification, 1995.

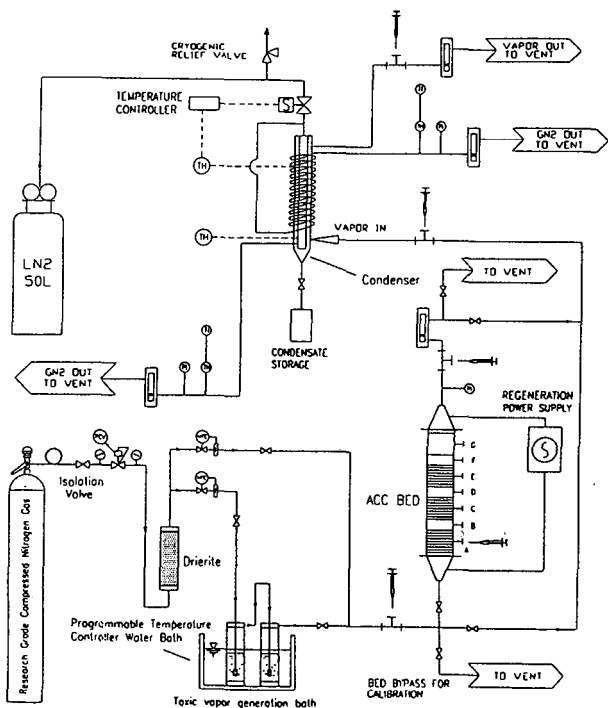## Acknowledgments

Figures

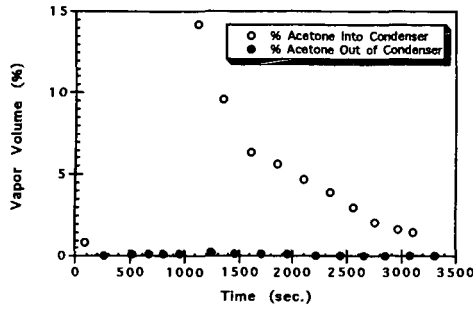Figure 1. Laboratory condenser set-up integrated with a fixed carbon adsorber.

Figure 2. Acetone outlet concentrations from desorption and condensation.
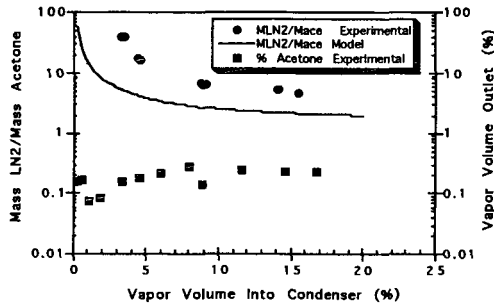

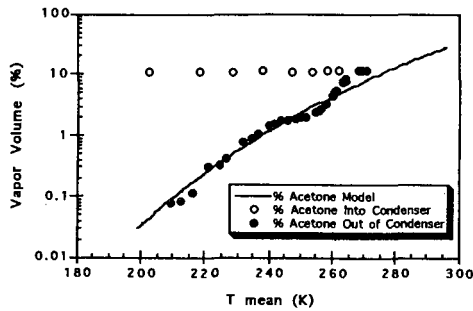**Figure 3.** LN2 requirements and condenser acetone outlet concentrations versus inlet concentrations.

Figure 4. Acetone outlet concentrations versus condenser equilibrium temperature.
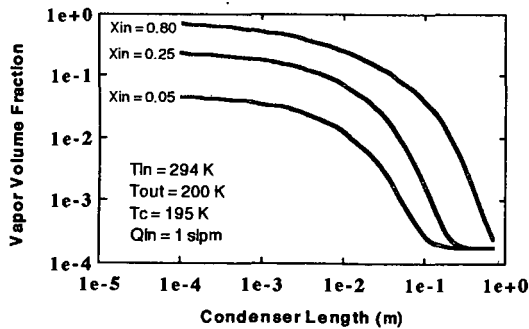

Figure 5. Modeled outlet acetone volume fractions for various condenser lengths. Xin is the inlet vapor volume fraction and Tc is the condensate film temperature.